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The following text is taken from the documents submitted by the applicant.

54 Method for producing organometallic fluorides

57 π-system-containing organometallic fluorides are obtained by reacting a fluorine-free organometallic halide with a tin fluoride with the general formula R^4_3SnF wherein the groups R^4 are the same or different and represent C₁ to C₁₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl.

Description

This invention relates to a method for producing π -system-containing organometallic fluorides that can be advantageously used as catalysts or catalyst components, in particular for polyolefin production.

Cyclopentadienyltitanium, -zirconium, and -hafnium complexes are used in combination with aluminoxane as catalysts for producing polyolefins. The corresponding di- and trichloride derivatives are particularly important as highly active olefin polymerization catalysts (*Adv. in Organomet. Chem.*, Vol. 18 (1988), pp. 99-149). Unbridged zirconocene difluorides are also known (*J. Chem. Soc. (A)* (1971), pp. 2225-2229; *J. Chem. Soc. Dalton Trans.* (1987), pp. 1463-1472).

It is known that the corresponding organometallic fluorides can be produced from transition metal chlorides and arsenic trifluoride by metathesis (*J. Chem. Soc. Dalton Trans.* (1990), p. 713). However, the reaction of pentamethylcyclopentadienyl-zirconium trichloride (or pentamethylcyclopentadienylhafnium trichloride) with arsenic trifluoride gives pentamethylcyclopentadienylarsenic dichloride in high yields. In addition to fluorine-to-chlorine exchange, the cyclopentadienyl ring is also transferred to the arsenic atom. Moreover, it is frequently quite difficult to separate excess arsenic trifluoride from the reaction product.

Therefore, the object was to find a method for producing π -system-containing organometallic fluorides that avoids the known disadvantages of the prior art.

Surprisingly, it was found that π -system-containing organometallic fluorides can be very easily synthesized on a preparative scale in very good yields using tin fluoride. To this end, a mixture of a tin fluoride and a fluorine-free organometallic halide is reacted in a solvent; this reaction can be run in technically favorable solvents such as aliphatic and aromatic hydrocarbons. The organometallic fluoride can be directly isolated after removal of all the volatile components. In addition, the tin fluoride can be easily recovered from the tin chloride product and reused as fluorinating agent.

This exchange of chlorine, bromine, or iodine with fluorine allows gradations in reactivity, primarily for influencing catalyst properties, to be obtained.

The invention relates to a method for producing π -system-containing organometallic fluorides with general formulas I, II, III, IV, V, and VI



wherein

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups R^1 are the same or different and represent hydrogen, C_1 to C_{20} alkyl, C_6 to C_{14} aryl, C_2 to C_{10} alkenyl, C_7 to C_{20} arylalkyl, or C_7 to C_{15} alkylaryl, or SiR^3_3 (wherein R^3 is C_1 to C_{10} alkyl), or neighboring R^1 groups form one or several aliphatic or aromatic ring systems with the atoms that connect said R^1 groups,

the groups R^5 are the same or different and represent C_1 to C_{10} alkyl, C_6 to C_{10} aryl, C_1 to C_{10} alkylaryl, NR^6_2 , OR^6 , SR^6 , $OSiR^6_3$, $>NR^6$, PR^6_2 , or $>PR^6$, wherein each R^6 is independently selected from hydrogen, C_1 to C_{10} alkyl, and C_6 to C_{10} aryl, and

$p = 1, 2, \text{ or } 3$, $o = 0, 1, \text{ or } 2$, $m = 4 - (p + o)$, $n = 1, 2, 3, 4, \text{ or } 5$, $(p + o) = 1, 2, \text{ or } 3$, $q = 2$ when $m = 1$, $p = 1$, and $R^5 = >NR^6$ or $>PR^6$, and otherwise $q = 1$;



wherein

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups R^1 are the same or different and represent hydrogen, C_1 to C_{20} alkyl, C_6 to C_{14} aryl, C_2 to C_{10} alkenyl, C_7 to C_{20} arylalkyl, or C_7 to C_{15} alkylaryl, or SiR^3_3 (wherein R^3 is C_1 to C_{10} alkyl), or neighboring R^1 groups form one or several aliphatic or aromatic ring systems with the atoms that connect said R^1 groups,

the groups R^2 are the same or different and represent hydrogen, C_1 to C_{20} alkyl, C_6 to C_{14} aryl, C_2 to C_{10} alkenyl, C_7 to C_{20} arylalkyl, or C_7 to C_{15}

alkylaryl, or neighboring R² groups form a ring system with the atoms that connect said R² groups,

the groups R⁵ are the same or different and represent C₁ to C₁₀ alkyl, C₆ to C₁₀ aryl, C₁ to C₁₀ alkylaryl, NR₂⁶, OR⁶, SR⁶, OSiR₃⁶, >NR⁶, PR₂⁶, or >PR⁶, wherein each R⁶ is independently selected from hydrogen, C₁ to C₁₀ alkyl, and C₆ to C₁₀ aryl,

B is carbon or silicon, and

k = 1, 2, or 3, **p** = 1 or 2, **o** = 0 or 1, **n** = 1, 2, 3, 4, or 5, (**p** + **o**) = 2, **q** = 2 when **m** = 1, **p** = 1, and R⁵ = >NR⁶ or >PR⁶, and otherwise **q** = 1;



wherein Cp, R¹, R², M, B, **k**, and **n** are defined as in formula II,

said method being characterized by reacting a compound with general formula VII, VIII, IX, X, XI, or XII



wherein Cp, R¹, R⁵, R⁶, M, **p**, **o**, **m**, **n**, and **q** are defined as in formula I and Y is chlorine, bromine, or iodine



wherein Cp, R¹, R², R⁵, R⁶, M, B, **k**, **p**, **o**, **n**, and **q** are defined as in formula II and Y is chlorine, bromine, or iodine





wherein Cp, R¹, R², B, Y, **k**, and **n** are defined as in formula II

in an inert solvent with a tin fluoride with general formula XIII



wherein the groups R⁴ are the same or different and represent C₁ to C₁₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl.

In preferred embodiments of formulas I through XII, M is titanium, zirconium, or hafnium; the groups R¹ are the same or different and represent hydrogen, C₁ to C₄ alkyl, C₆ to C₁₂ aryl, C₂ to C₆ alkenyl, C₇ to C₁₅ arylalkyl, C₇ to C₁₅ alkylaryl, or SiR³₃ (wherein R³ is C₁ to C₄ alkyl) or neighboring R¹ groups form an aliphatic or aromatic ring system; the groups R² are the same or different and represent hydrogen, C₁ to C₄ alkyl, C₆ to C₁₂ aryl, C₂ to C₆ alkenyl, C₇ to C₁₅ arylalkyl, or C₇ to C₁₅ alkylaryl; the groups R⁵ are the same or different and represent C₁ to C₁₀ alkyl or >NR⁶; and **k** = 1 or 2, **p** = 2 or 3, **o** = 0, and **q** = 1; and Y in formulas VII through XII is preferably chlorine.

In particularly preferred embodiments, M is zirconium or titanium; R¹ is hydrogen, C₁ to C₄ alkyl, C₆ to C₁₀ aryl, or SiR³₃ wherein R³ is C₁ to C₄ alkyl, or neighboring R¹ groups form a substituted or unsubstituted, aliphatic or aromatic six-membered ring; R² is C₁ to C₄ alkyl or phenyl; **k** = 1 when B is silicon and **k** = 2 when B is carbon; **p** = 2; **o** = 0; and **q** = 1.

R⁴ in formula XIII is preferably C₁ to C₄ alkyl and particularly methyl.

In all formulas, "alkyl" denotes linear or branched alkyl.

The reaction of a compound with formula VII or VIII to give a compound with formula I or II is preferred. Titanium, zirconium, and hafnium can occur in formulas I through XII in an oxidation state of +3 or +4.

The following examples serve to illustrate the organometallic fluorides described in general formulas I through VI in more detail, but are not to be construed as all inclusive.

ethylenebis(indenyl)zirconium difluoride

ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium difluoride

ethylenebis(2-methylindenyl)zirconium difluoride

ethylenebis(2,4-dimethylindenyl)zirconium difluoride

dimethylsilandiylbis(2-methyl-4,5-benzoindenyl)zirconium difluoride

dimethylsilandiylbis(2-methyl-4,6-diisopropylindenyl)zirconium difluoride

dimethylsilandiylbis(2-methyl-4-phenylindenyl)zirconium difluoride

dimethylsilandiylbis(2-ethyl-4-phenylindenyl)zirconium difluoride

dimethylsilandiylbis(2-methyl-4-(1-naphthyl)indenyl)zirconium difluoride

dimethylsilandiylbis(indenyl)zirconium difluoride

dimethylsilandiylbis(2-methyl-4-ethylindenyl)zirconium difluoride

dimethylsilandiylbis(2-methyl-4-isopropylindenyl)zirconium difluoride

dimethylsilandiylbis(2-methyl-4-methylindenyl)zirconium difluoride

dimethylsilandiylbis(2-ethyl-4-methylindenyl)zirconium difluoride

dimethylsilandiylbis(2-methyl- α -acenaphth-1-indenyl)zirconium difluoride

phenylmethylsilandiylbis(2-methyl-4-phenylindenyl)zirconium difluoride

phenylmethylsilandiylbis(2-methylindenyl)zirconium difluoride

ethylenebis(2-methyl-4,5-benzoindenyl)zirconium difluoride

ethylenebis(2-methyl-4,6-diisopropylindenyl)zirconium difluoride

ethylenebis(2-methyl-4-phenylindenyl)zirconium difluoride

ethylenebis(2-ethyl-4-phenylindenyl)zirconium difluoride

ethylenebis(2-methyl-4-(1-naphthyl)indenyl)zirconium difluoride

ethylenebis(indenyl)zirconium difluoride

ethylenebis(2-methyl-4-ethylindenyl)zirconium difluoride

ethylenebis(2-methyl-4-isopropylindenyl)zirconium difluoride

ethylenebis(2-methyl-4-methylindenyl)zirconium difluoride

ethylenebis(2-ethyl-4-methylindenyl)zirconium difluoride

ethylenebis(2-methyl- α -acenaphth-1-indenyl)zirconium difluoride

bis(2-methyl-4,5-benzoindenyl)zirconium difluoride

bis(2-methyl-4,6-diisopropylindenyl)zirconium difluoride

bis(2-methyl-4-phenylindenyl)zirconium difluoride

bis(2-ethyl-4-phenylindenyl)zirconium difluoride
bis(2-methyl-4-(1-naphthyl)indenyl)zirconium difluoride
bis(indenyl)zirconium difluoride
bis(2-methyl-4-ethylindenyl)zirconium difluoride
bis(2-methyl-4-isopropylindenyl)zirconium difluoride
bis(2-methyl-4-methylindenyl)zirconium difluoride
bis(2-ethyl-4-methylindenyl)zirconium difluoride
bis(2-methyl- α -acenaphth-1-indenyl)zirconium difluoride
bis(*n*-butylcyclopentadienyl)zirconium difluoride
bis(cyclopentadienyl)zirconium difluoride
bis(pentamethylcyclopentadienyl)zirconium difluoride
cyclopentadienylzirconium trifluoride
pentamethylcyclopentadienylzirconium trifluoride
(2-methyl-4,5-benzoindenyl)zirconium trifluoride
(2-methyl-4,6-diisopropylindenyl)zirconium trifluoride
(2-methyl-4-phenylindenyl)zirconium trifluoride
(2-ethyl-4-phenylindenyl)zirconium trifluoride
(2-methyl-4-(1-naphthyl)indenyl)zirconium trifluoride
indenylzirconium trifluoride
(2-methyl-4-ethylindenyl)zirconium trifluoride
(2-methyl-4-isopropylindenyl)zirconium trifluoride
(2-methyl-4-methylindenyl)zirconium trifluoride
(2-ethyl-4-methylindenyl)zirconium trifluoride
(2-methyl- α -acenaphth-1-indenyl)zirconium trifluoride
(*n*-butylcyclopentadienyl)zirconium trifluoride
isopropylidene(9-fluorenyl)cyclopentadienylzirconium difluoride
diphenylmethylene(9-fluorenyl)cyclopentadienylzirconium difluoride
phenylmethylmethylene(9-fluorenyl)cyclopentadienylzirconium difluoride
dimethylsilandiyl(9-fluorenyl)cyclopentadienylzirconium difluoride
isopropylidene(9-fluorenyl)(3-methylcyclopentadienyl)zirconium difluoride
diphenylmethylene(9-fluorenyl)(3-methylcyclopentadienyl)zirconium difluoride
phenylmethylmethylene(9-fluorenyl)(3-methylcyclopentadienyl)zirconium difluoride
dimethylsilandiyl(9-fluorenyl)(3-methylcyclopentadienyl)zirconium difluoride
isopropylidene(9-fluorenyl)(3-isopropylcyclopentadienyl)zirconium difluoride
diphenylmethylene(9-fluorenyl)(3-isopropylcyclopentadienyl)zirconium difluoride
phenylmethylmethylene(9-fluorenyl)(3-isopropylcyclopentadienyl)zirconium difluoride

dimethylsilandiyl(9-fluorenyl)(3-isopropylcyclopentadienyl)zirconium difluoride
isopropylidene(2,7-di-*tert*-butyl-9-fluorenyl)cyclopentadienylzirconium difluoride
diphenylmethylene(2,7-di-*tert*-butyl-9-fluorenyl)cyclopentadienylzirconium difluoride
phenylmethylmethylene(2,7-di-*tert*-butyl-9-fluorenyl)cyclopentadienylzirconium
difluoride
dimethylsilandiyl(2,7-di-*tert*-butyl-9-fluorenyl)cyclopentadienylzirconium difluoride
ethylenebis(indenyl)titanium difluoride
ethylenebis(4,5,6,7-tetrahydroindenyl)titanium difluoride
ethylenebis(2-methylindenyl)titanium difluoride
dimethylsilandiylbis(indenyl)titanium difluoride
bis(indenyl)titanium difluoride
bis(cyclopentadienyl)titanium difluoride
bis(pentamethylcyclopentadienyl)titanium difluoride
cyclopentadienyltitanium trifluoride
pentamethylcyclopentadienyltitanium trifluoride
indenyltitanium trifluoride
(*n*-butylcyclopentadienyl)titanium trifluoride
isopropylidene(9-fluorenyl)cyclopentadienyltitanium difluoride
ethylenebis(indenyl)hafnium difluoride
ethylenebis(4,5,6,7-tetrahydroindenyl)hafnium difluoride
ethylenebis(2-methylindenyl)hafnium difluoride
dimethylsilandiylbis(indenyl)hafnium difluoride
bis(indenyl)hafnium difluoride
bis(cyclopentadienyl)hafnium difluoride
bis(pentamethylcyclopentadienyl)hafnium difluoride
cyclopentadienylhafnium trifluoride
pentamethylcyclopentadienylhafnium trifluoride
indenylhafnium trifluoride
(*n*-butylcyclopentadienyl)hafnium trifluoride
isopropylidene(9-fluorenyl)cyclopentadienylhafnium difluoride
bis(cyclopentadienyl)titanium fluoride
bis(methylcyclopentadienyl)titanium fluoride
bis(pentamethylcyclopentadienyl)titanium fluoride
[(Me₃SiC₅H₄)Ti(F)Nt-Bu]₂

The organometallic halides required as starting compounds are commercially available, or can be produced by methods known from the literature. The tin fluorides with formula XIII required as starting materials can be produced by methods known from the literature (*Ber. Dtsch. Chem. Ges.* (1918), Vol. 51, p. 1447).

The reaction is carried out in an inert solvent such as hexane, toluene, or methylcyclohexane, preferably in toluene.

The reaction can be run at temperatures ranging from -50 to 120°C, preferably 25 to 100°C.

The molar ratio of the reactants is determined by the number of halogen atoms to be substituted in the organometallic compound. While an excess of tin fluoride with formula XIII can be used, the tin fluoride with formula XIII is preferably used in stoichiometric quantities.

After the reaction is completed, the volatile components are removed and the solvent reused. The tin fluoride with formula XIII may be recovered from the resulting tin halide (*Ber. Dtsch. Chem. Ges.* (1918), Vol. 51, p. 1447).

The organometallic fluorides with formulas I, II, III, IV, V, and VI are obtained in very good yields, preferably greater than 85%. Further purification can generally be omitted.

The inventive method for producing organometallic fluorides is characterized in that it is technically simple to perform and requires commonly available starting materials. The solvent can be reused and the fluorinating agent can be recovered.

Moreover, the method according to the invention enables the production of certain π -system-containing organometallic fluorides not available using previous methods. The present invention thus applies to the following compounds with formulas I, II, III, IV, V, and VI



in which

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups R¹ are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or SiR³₃ (wherein R³ is C₁ to C₁₀ alkyl) or neighboring R¹ groups form one or several aliphatic or aromatic ring systems with the atoms that join said R¹ groups,

the groups R⁵ are the same or different and represent C₁ to C₁₀ alkyl, C₆ to C₁₀ aryl, C₁ to C₁₀ alkylaryl, NR⁶₂, OR⁶, SR⁶, OSiR⁶₃, NR⁶, PR⁶₂, or PR⁶ (wherein the groups R⁶ are the same or different and represent hydrogen, C₁ to C₁₀ alkyl, or C₆ to C₁₀ aryl), and

p = 1 or 3, **o** = 0, 1, or 2, **m** = 4 - (**p** + **o**), **n** = 1, 2, 3, 4, or 5, (**p** + **o**) = 1, 2, or 3, **q** = 2 when **m** = 1, **p** = 1, and R⁵ = >NR⁶ or >PR⁶, and otherwise **q** = 1;



in which

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

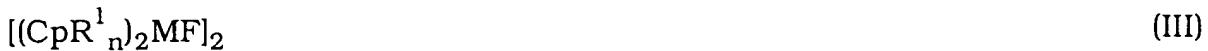
the groups R¹ are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or SiR³₃ (wherein R³ is C₁ to C₁₀ alkyl), or neighboring R¹ groups form one or several aliphatic or aromatic ring systems with the atoms that join said R¹ groups,

the groups R² are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or neighboring R² groups form a ring system with the atoms that join said R² groups,

the groups R⁵ are the same or different and represent C₁ to C₁₀ alkyl, C₆ to C₁₀ aryl, C₁ to C₁₀ alkylaryl, NR⁶₂, OR⁶, SR⁶, OSiR⁶₃, >NR⁶, PR⁶₂, or >PR⁶, (wherein the groups R⁶ are the same or different and represent hydrogen, C₁ to C₁₀ alkyl, or C₆ to C₁₀ aryl),

B is carbon or silicon, and

k = 1, 2, or 3, **p** = 1 or 2, **o** = 0 or 1, **n** = 1, 2, 3, 4, or 5, (**p** + **o**) = 2, **q** = 2 when **m** = 1, **p** = 1, and R⁵ = >NR⁶ or >PR⁶, and otherwise **q** = 1;



in which Cp, R¹, R², M, B, k, and n are defined as in formula II.

In preferred embodiments of formulas I through VI,

M is titanium, zirconium, or hafnium,

the groups R¹ are the same or different and represent hydrogen, C₁ to C₄ alkyl, C₆ to C₁₂ aryl, C₂ to C₆ alkenyl, C₇ to C₁₅ arylalkyl, C₇ to C₁₅ alkylaryl, or SiR³₃ (wherein R³ is C₁ to C₄ alkyl), or neighboring R¹ groups form an aliphatic or aromatic ring system,

the groups R² are the same or different and represent hydrogen, C₁ to C₄ alkyl,

C₆ to C₁₂ aryl, C₂ to C₆ alkenyl, C₇ to C₁₅ arylalkyl, or C₇ to C₁₅ alkylaryl,

the groups R⁵ are the same or different and represent C₁ to C₁₀ alkyl or >NR⁶,

B is carbon or silicon, and

k = 1 or 2 and q = 1.

In formula II, p is preferably 2, o = 0, and q = 1.

In particularly preferred embodiments, M is zirconium or titanium; R¹ is hydrogen, C₁ to C₄ alkyl, C₆ to C₁₂ aryl, or SiR³₃ (wherein R³ is C₁ to C₄ alkyl), or neighboring R¹ groups form a substituted or unsubstituted, aliphatic or aromatic six-membered ring; R² is C₁ to C₄ alkyl or phenyl; k = 1 when B is silicon; k = 2 when B is carbon; and q = 1.

The π-system-containing organometallic fluorides according to the invention are very thermally stable and are therefore particularly suitable for catalysts that are used at high temperatures.

The following examples explain the invention in additional detail.

Examples

Example A

Pentamethylcyclopentadienylzirconium trifluoride

A mixture of 5.0 g (15.0 mmol) pentamethylcyclopentadienylzirconium trichloride and 8.2 g (45.1 mmol) Me_3SnF was combined with 80 mL toluene and stirred at room temperature. A slightly turbid solution formed after 0.5 hr. The mixture was heated at the boiling point for 0.1 hr to complete the reaction. The mixture was allowed to cool and undissolved impurities were filtered off. The colorless solid remaining after evaporation of all volatile components was washed with *n*-hexane and dried under vacuum. Yield: 4.0 g (94%), mp > 350°C, $^1\text{H-NMR}$ (C_6D_6): δ = 2.02 (s); $^{19}\text{F-NMR}$ (C_6D_6): δ = 97.5 (m), -26.3 (m), -50.7 (m), -72.7 (m); EI-MS (70 eV): m/z 831 ($\text{C}_{30}\text{H}_{45}\text{F}_8\text{Zr}_3$, 100%).

— Elemental analysis: $\text{C}_{10}\text{H}_{15}\text{F}_3\text{Zr}$ (283.45), Found: C 42.2, H 5.5, F 19.0; Reported: C 42.4, H 5.3, F 20.1.

Example B

Pentamethylcyclopentadienylhafnium trifluoride

A mixture of 4.6 g (11.0 mmol) pentamethylcyclopentadienylhafnium trichloride and 6.0 g (32.9 mmol) $[\text{Me}_3\text{SnF}]$ was combined with 80 mL toluene and was reacted and worked up as described in Example A. Yield: 3.7 g (93%), mp > 350°C, $^1\text{H-NMR}$ (C_6D_6): δ = 2.07 (s); $^{19}\text{F-NMR}$ (C_6D_6): δ = 41.8 (m), -54.0 (m), -77.3 (m), -97.8 (m); EI-MS (70 eV): m/z 1093 ($\text{C}_{30}\text{H}_{45}\text{F}_8\text{Hf}_3$, 40%).

— Elemental analysis: $\text{C}_{10}\text{H}_{15}\text{F}_3\text{Hf}$ (370.71), Found: C 31.1, H 4.3, F 15.2; Reported: C 32.4, H 4.1, F 15.4.

Example C

Bis(pentamethylcyclopentadienyl)zirconium difluoride

A mixture of 2.00 g (4.6 mmol) bis(pentamethylcyclopentadienyl)zirconium dichloride and 1.69 g (9.24 mmol) trimethylzinc fluoride was combined with 40 mL toluene and heated under reflux for 0.5 hr.

After cooling, all volatile components were removed under vacuum. The residue was subjected to vacuum for an additional hour at 80°C.

The remaining white solid was washed with a small amount of hexane and dried under vacuum. Bis(pentamethylcyclopentadienyl)zirconium difluoride was obtained in a yield of 89% (1.64 g). The melting point was 205°C.

Mass spectrum: m/z = 398 molecular peak with correct isotope distribution

^1H -NMR (C_6D_6 , TMS external): δ = 1.83 ppm (triplet)

^{19}F -NMR (C_6D_6 , CFCl_3 external): δ = +28.61 ppm

IR spectrum: 1260, 1092, 1021; 800, 548, 535, 398, 376 cm^{-1} ; correct elemental analysis

Example D

$[(\text{Me}_3\text{SiC}_5\text{H}_4)\text{Ti}(\text{F})\text{NtBu}]_2$

A mixture of 1.02 g (2.75 mmol) $(\text{Me}_3\text{SiC}_5\text{H}_4)\text{Ti}(\text{Cl})\text{NtBu}$ -pyridine and 0.50 g (2.75 mmol) Me_3SnF was combined with 50 mL toluene and stirred at 90°C for 0.5 hr. The mixture was allowed to cool to room temperature and all volatile components were removed under vacuum. The remaining red solid was taken up in a small amount of hexane. After cooling to -20°C, $[(\text{Me}_3\text{SiC}_5\text{H}_4)\text{Ti}(\text{F})\text{NtBu}]_2$ was obtained after 12 hr in the form of red crystals in a yield of 95% (0.72 g) and with a melting point of 218°C.

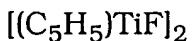
^1H -NMR (C_6D_6 , TMS external): δ = 0.31 (s, 9H, Me_3Si), 1.05 (s, 9H, Bu), 5.95 (dd, 2H), 6.99 (dd, 2H) ppm

^{19}F -NMR (C_6D_6 , CFCl_3 external): δ = 109.5 ppm

Mass spectrum: m/z = 550 dimer

IR spectrum: 840, 801, 623, 595 cm⁻¹

Example E



A mixture of $[(C_5H_5)TiCl]_2$ (0.64 g, 1.5 mmol) and Me_3SnF (0.55 g, 3 mmol) was combined with 60 mL toluene and stirred at room temperature. The solvent was removed under vacuum after all the Me_3SnF had gone into solution. The residue was crystallized from THF/hexane as green crystals.

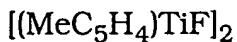
Yield: 0.53 g (90%), melting point: 228°C

IR: 3091, 1093, 793, 471, 380 cm⁻¹

Mass spectrum: m/z = 197 M⁺

Correct elemental analysis

Example F



The synthesis was analogous to that for $[(C_5H_5)TiF]_2$. Yield 92%, melting point 94.5°C, mass spectrum: m/z = 225 M⁺.

Example G



1.06 g (3 mmol) $(C_5Me_5)_2TiCl$ was dissolved in 30 mL toluene and added dropwise to a suspension of 0.55 g (3 mmol) Me_3SnF in 30 mL toluene. The solid disappeared after stirring for three hours at room temperature. The solvent was then removed under vacuum and the residue was sublimed. 0.88 g (88%) of a green solid was obtained. Melting point: 184°C, mass spectrum: m/z = 337, M-Me.

Polymerization Examples

All glass instruments were heated in vacuo and flushed with argon. All operations were carried out with exclusion of moisture and oxygen in Schlenk flasks. The solvents used were freshly distilled over Na/K alloy under argon and kept in Schlenk flasks.

The aluminum determination was performed after hydrolysis by water and sulfuric acid by complexometric titration according to Schwarzenbach.

Toluene-soluble methylaluminoxane was used for the polymerization examples as the 10% toluene solution from Schering AG, which contained 36 mg Al/mL by aluminum determination. The average degree of oligomerization by freezing point depression in benzene was $n = 20$.

Example 1

A dry 1.5 dm³ stirred reactor was flushed with nitrogen to remove oxygen, filled with 0.9 dm³ inert diesel oil (boiling point 100–120°C), and heated to 70°C. In parallel with this operation, [1.0 mg] bis(pentamethylcyclopentadienyl)zirconium difluoride was dissolved in a 10 wt% solution of methylaluminoxane in toluene (12 mmol Al) and preactivated by stirring. The polymerization was initiated by injecting the catalyst solution and applying a pressure of 7 bar ethylene. After 1 hr at 70°C, the reactor was depressurized and the polymer was filtered from the suspension and dried for 12 hr in a vacuum drying oven. The result was [60.9 g] polyethylene powder, corresponding to 3480 g-PE/mmol-Zr/hr/bar, having a viscosity number of 150 cm³/g. The molar mass distribution as determined by gel permeation chromatography was M_w/M_n = 2.6.

Example 2

Example 1 was repeated using 11.0 mg pentamethylcyclopentadienylzirconium trifluoride. The result was 20 g polyethylene powder, corresponding to 70 g-PE/mmol-Zr/hr/bar, having a viscosity number of 600 cm³/g. The molar mass distribution as determined by gel permeation chromatography was M_w/M_n = 2.7.

Comparative Example

The polymerization of Example 1 was repeated, except that 0.50 mg bis(pentamethylcyclopentadienyl)zirconium dichloride was used as catalyst. Under otherwise identical conditions, the result was 21 g polyethylene, corresponding to 2600 g-PE/mmol-Zr/hr/bar, having a viscosity number of 200 cm³/g. The molar mass distribution as determined by gel permeation chromatography was M_w/M_n = 2.6.

Patent Claims

1. Method for producing π -system-containing organometallic fluorides with general formulas I, II, III, IV, V, and VI



wherein

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups R¹ are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or SiR³₃ (wherein R³ is C₁ to C₁₀ alkyl), or neighboring R¹ groups form one or several aliphatic or aromatic ring systems with the atoms that connect said R¹ groups,

the groups R⁵ are the same or different and represent C₁ to C₁₀ alkyl, C₆ to C₁₀ aryl, C₁ to C₁₀ alkylaryl, NR⁶₂, OR⁶, SR⁶, OSiR⁶₃, >NR⁶, PR⁶₂, or >PR⁶, wherein each R⁶ is independently selected from hydrogen, C₁ to C₁₀ alkyl, and C₆ to C₁₀ aryl, and

p = 1, 2, or 3, **o** = 0, 1, or 2, **m** = 4 - (**p** + **o**), **n** = 1, 2, 3, 4, or 5, (**p** + **o**) = 1, 2, or 3, **q** = 2 when **m** = 1, **p** = 1, and R⁵ = >NR⁶ or >PR⁶, and otherwise **q** = 1;



wherein

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group.

the groups R¹ are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or SiR³₃ (wherein R³ is C₁ to C₁₀ alkyl), or neighboring R¹ groups form one or several aliphatic or aromatic ring systems with the atoms that connect said R¹ groups,

the groups R² are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or neighboring R² groups form a ring system with the atoms that connect said R² groups,

the groups R⁵ are the same or different and represent C₁ to C₁₀ alkyl, C₆ to C₁₀ aryl, C₁ to C₁₀ alkylaryl, NR⁶₂, OR⁶, SR⁶, OSiR⁶₃, >NR⁶, PR⁶₂, or >PR⁶, wherein each R⁶ is independently selected from hydrogen, C₁ to C₁₀ alkyl, and C₆ to C₁₀ aryl,

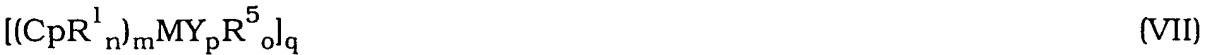
B is carbon or silicon, and

k = 1, 2, or 3, **p** = 1 or 2, **o** = 0 or 1, **n** = 1, 2, 3, 4, or 5, (**p** + **o**) = 2, **q** = 2 when **m** = 1, **p** = 1, and R⁵ = >NR⁶ or >PR⁶, and otherwise **q** = 1;



wherein Cp, R¹, R², M, B, **k**, and **n** are defined as in formula II,

said method being characterized by reacting a compound with general formula VII, VIII, IX, X, XI, or XII



wherein Cp, R¹, R⁵, R⁶, M, **p**, **o**, **m**, **n**, and **q** are defined as in formula I and Y is chlorine, bromine, or iodine



wherein Cp, R¹, R², R⁵, R⁶, M, B, **k**, **p**, **o**, **n**, and **q** are defined as in formula II
and Y is chlorine, bromine, or iodine



wherein Cp, R¹, R², B, Y, **k**, and **n** are defined as in formula II,

in an inert solvent with a tin fluoride with general formula XIII



wherein the groups R⁴ are the same or different and represent C₁ to C₁₀ alkyl,
C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅
alkylaryl.

2. Method according to Claim 1, characterized in that M in formulas I, II, III, IV, V, VI, VII, VIII, IX, X, XI, and XII represents titanium, zirconium, or hafnium.
3. Method according to Claim 1, characterized in that Y in formulas VII, VIII, IX, X, XI, and XII represents chlorine.
4. Method according to Claim 1, characterized in that R³ in formula XIII represents C₁ to C₁₀ alkyl.
5. Use of a compound with formula XIII



to produce organometallic fluoride with general formula I, II, III, IV, V, or VI



wherein

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups R¹ are the same or different and represent hydrogen, C₁ to C₂₀

alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or SiR³₃ (wherein R³ is C₁ to C₁₀ alkyl), or neighboring R¹ groups form one or several aliphatic or aromatic ring systems with the atoms that connect said R¹ groups,

the groups R⁵ are the same or different and represent C₁ to C₁₀ alkyl, C₆ to C₁₀ aryl, C₁ to C₁₀ alkylaryl, NR⁶₂, OR⁶, SR⁶, OSiR⁶₃, >NR⁶, PR⁶₂, or >PR⁶, wherein each R⁶ is independently selected from hydrogen, C₁ to C₁₀ alkyl, and C₆ to C₁₀ aryl, and

p = 1, 2, or 3, **o** = 0, 1, or 2, **m** = 4 - (**p** + **o**), **n** = 1, 2, 3, 4, or 5, (**p** + **o**) = 1, 2, or 3, **q** = 2 when **m** = 1, **p** = 1, and R⁵ = >NR⁶ or >PR⁶, and otherwise **q** = 1;



wherein

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups R¹ are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or SiR³₃ (wherein R³ is C₁ to C₁₀ alkyl), or neighboring R¹ groups form one or several aliphatic or aromatic ring systems with the atoms that connect said R¹ groups,

the groups R² are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or neighboring R² groups form a ring system with the atoms that connect said R² groups,

the groups R⁵ are the same or different and represent C₁ to C₁₀ alkyl, C₆ to C₁₀ aryl, C₁ to C₁₀ alkylaryl, NR⁶₂, OR⁶, SR⁶, OSiR⁶₃, >NR⁶, PR⁶₂, or >PR⁶, wherein each R⁶ is independently selected from hydrogen, C₁ to C₁₀ alkyl, and C₆ to C₁₀ aryl,

B is carbon or silicon, and

k = 1, 2, or 3, **p** = 1 or 2, **o** = 0 or 1, **n** = 1, 2, 3, 4, or 5, (**p** + **o**) = 2, **q** = 2 when
m = 1, **p** = 1, and R⁵ = >NR⁶ or >PR⁶, and otherwise **q** = 1;



wherein Cp, R¹, R², M, B, **k**, and **n** are defined as in formula II.

6. Compound with formula I



in which

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups R¹ are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or SiR³₃ (wherein R³ is C₁ to C₁₀ alkyl) or neighboring R¹ groups form one or several aliphatic or aromatic ring systems with the atoms that join said R¹ groups,

the groups R⁵ are the same or different and represent C₁ to C₁₀ alkyl, C₆ to C₁₀ aryl, C₁ to C₁₀ alkylaryl, NR⁶₂, OR⁶, SR⁶, OSiR⁶₃, NR⁶, PR⁶₂, or PR⁶ (wherein the groups R⁶ are the same or different and represent hydrogen, C₁ to C₁₀ alkyl, or C₆ to C₁₀ aryl), and

p = 1 or 3, **o** = 0, 1, or 2, **m** = 4 - (**p** + **o**), **n** = 1, 2, 3, 4, or 5, (**p** + **o**) = 1, 2, or 3, **q** = 2 when **m** = 1, **p** = 1, and R⁵ = >NR⁶ or >PR⁶, and otherwise **q** = 1.

7. Compound according to Claim 6, characterized in that M represents titanium, zirconium, or hafnium.

8. Compound with formula II



in which

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups R¹ are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or SiR³₃ (wherein R³ is C₁ to C₁₀ alkyl), or neighboring R¹ groups form one or several aliphatic or aromatic ring systems with the atoms that join said R¹ groups,

the groups R² are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or neighboring R² groups form a ring system with the atoms that join said R² groups,

the groups R⁵ are the same or different and represent C₁ to C₁₀ alkyl, C₆ to C₁₀ aryl, C₁ to C₁₀ alkylaryl, NR⁶₂, OR⁶, SR⁶, OSiR⁶₃, >NR⁶, PR⁶₂, or >PR⁶, (wherein the groups R⁶ are the same or different and represent hydrogen, C₁ to C₁₀ alkyl, or C₆ to C₁₀ aryl),

B is carbon or silicon, and

k = 1, 2, or 3, p = 1 or 2, o = 0 or 1, n = 1, 2, 3, 4, or 5, (p + o) = 2, q = 2 when m = 1, p = 1, and R⁵ = >NR⁶ or >PR⁶, and otherwise q = 1.

9. Compound according to Claim 8, characterized in that M represents titanium, zirconium, or hafnium.

10. Compounds with formulas III, IV, V, and VI



in which

M is titanium, zirconium, hafnium, vanadium, niobium, or tantalum,

Cp is the cyclopentadienyl group,

the groups R¹ are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or SiR₃³ (wherein R³ is C₁ to C₁₀ alkyl), or neighboring R¹ groups form one or several aliphatic or aromatic ring systems with the atoms that join said R¹ groups,

the groups R² are the same or different and represent hydrogen, C₁ to C₂₀ alkyl, C₆ to C₁₄ aryl, C₂ to C₁₀ alkenyl, C₇ to C₂₀ arylalkyl, or C₇ to C₁₅ alkylaryl, or neighboring R² groups form a ring system with the atoms that join said R² groups,

B is carbon or silicon, and

k = 1, 2, or 3 and **n** = 1, 2, 3, 4, or 5.